Competition between electrochemical advanced oxidation and electrochemical hypochlorination of acetaminophen at boron-doped diamond and ruthenium dioxide based anodes

Jordache Boudreau, Dorin Bejan, and Nigel J. Bunce

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Abstract: This work was undertaken to distinguish four pathways for the electrochemical oxidation of acetaminophen as a model organic substrate: (*i*) direct electron transfer from the substrate to the anode, (*ii*) reaction of the substrate with $HO^{\bullet}$ at boron-doped diamond anodes, (*iii*) non-radical (two-electron) oxidation of the substrate at Ti/RuO_2 anodes, and (*iv*) electrochemical hypochlorination if Cl^- is present. Pathway (*i*) was isolated as a slow reaction when boron-doped diamond (BDD) was used as the anode in the range of water stability, whereas in the corresponding reaction with Ti/RuO_2 only pathway (*iii*) could be detected. Pathway (*ii*) predominated for BDD in the potential range of water oxidation, and was the only mechanism leading to mineralization of the substrate. Comparison between chemical hypochlorination and electrochemical oxidation at Ti/RuO_2 in the presence of chloride ion indicated that the latter process principally involves mediated hypochlorination. Oxidation at boron-doped diamond anodes in the presence of chloride was the most complex mechanistically, with competition between hypochlorination and the electrochemical "advanced oxidation process"; this led to the formation of chlorinated byproducts. The observation of mineralization under these conditions demonstrated cross-over between reaction pathways (*ii*) and (*iv*), even though hypochlorination appeared to be the initial pathway for loss of acetaminophen. The presence of chloride ion did not significantly retard mineralization of acetaminophen in the initial stages of oxidation, but significantly increased the energy requirement for complete mineralization. The results are discussed in the context of the use of electrochemical oxidation in waste management.

Key words: mineralization, electrochemical hypochlorination, electrochemical advanced oxidation, boron-doped diamond anode, acetaminophen.

Résumé : On a entrepris ce travail dans le but d'établir une distinction entre les quatre voies réactionnelles lors de l'oxydation électrochimique de l'acétaminophène utilisé comme substrat organique modèle : (*i*) transfert d'électron direct du substrat à l'anode; (*ii*) réaction du substrat avec le $HO^{\bullet}$ au niveau des anodes de diamant dopées au bore; (*iii*) oxydation non radicalaire à deux électrons du substrat au niveau des anodes de Ti/RuO_2 et (*iv*) hypochloruration électrochimique si l'anion Cl^- est présent. La voie réactionnelle (*i*) a été détectée sous la forme de réaction lente quand on utilise du diamant dopé au bore (DDB) comme anode dans la plage de stabilité de l'eau alors que pour la réaction correspondante avec des anodes de Ti/RuO_2 on n'a détecté que la voie (*iii*). La voie (*ii*) est prédominante pour le DDB dans la plage de potentiel d'oxydation de l'eau et c'est le seul mécanisme qui conduit à la minéralisation du substrat. Une comparaison entre l'hypochloruration chimique et l'oxydation électrochimique avec des anodes de Ti/RuO_2, en présence d'ion chlorure, indique que le deuxième processus implique une hypochloruration catalysée. L'oxydation au niveau des anodes de diamant dopées au bore, en présence d'ion chlorure, est la réaction la plus complexe d'un point de vue mécanistique et elle implique une compétition entre l'hypochloruration et le processus d'oxydation électrochimique avancée; ceci conduit à la formation de sous-produits chlorés. L'observation d'une minéralisation dans ces conditions a permis de démontrer qu'il se produit un croisement entre les voies réactionnelles (*ii*) et (*iv*), même si l'hypochloruration semblait être la voie initiale pour la perte de l'acétaminophène. La présence d'ion chlorure ne retarde pas d'une façon significative la minéralisation de l'acétaminophène dans les étapes initiales de l'oxydation, mais elle augmente considérablement l'énergie requise pour arriver à une minéralisation complète. On discute des résultats dans le contexte d'une utilisation de l'oxydation électrochimique dans la gestion des déchets.

Mots-clés : minéralisation, hypochloruration électrochimique, oxydation électrochimique avancée, anode de diamant dopé au bore, acétaminophène.

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Introduction

Electrochemical oxidation of organic-contaminated wastewaters has received considerable research attention as a possible treatment method.[1–7] Much of this effort has focused on anodes with a high overpotential for oxygen evolution (inactive anodes), notably β-PbO_2, Ti/SnO_2, and boron-doped diamond (BDD), which are especially effective at producing sorbed hydroxyl radicals, also called "physisorbed active oxygen".[8,9] These methods have been termed electrochemical advanced oxidation processes (EAOPs)[10–12] by analogy with conventional "advanced oxidation processes" (AOPs), which also involve hydroxyl radicals. Hydroxyl radicals have high and indiscriminate reactivity towards most organic compounds through addition and (or) hydrogen abstraction reactions,[13] leading to complete oxidation (mineralization) of recalcitrant organic contaminants by EAOP, or partial oxidation to render them more amenable to conventional biological oxidation.

Electrochemical oxidation of organic substrates is accelerated in the presence of chloride ion, which is a common constituent of industrial waste streams.[14–17] Chloride can be oxidized electrochemically to hypochlorous acid or hypochlorite ion, depending on the pH; the resulting free available chlorine (FAC) can effect electrochemical hypochlorination (EH) because FAC is both a chlorinating and an oxidizing agent. Hypochlorination does not lead to mineralization and may produce chlorinated byproducts that are more recalcitrant to remediation than the original contaminants. EH should predominate over EAOP at "active" anodes based on Ti/IrO_2 and Ti/RuO_2, which function as oxidizing agents by a "higher oxide" (MO_{n+1}) mechanism,[18–20] and which also promote efficient conversion of chloride to FAC.[21]

In principle, an organic contaminant might be electrochemically oxidized by several different reaction pathways when chloride ion is present. These are direct electron transfer from the substrate to the anode, EAOP by reaction of the substrate with $HO^{\bullet}$ at inactive anodes, non-radical (two-electron) oxidation of the substrate by MO_{n+1} at active anodes, and EH if Cl^- is present.

We recently explored the relationship between some of these mechanisms using the antibiotic sulfamethoxazole (SMX) as a test substrate.[22] Most of the work was carried out using BDD anodes, at which EH and EAOP should occur competitively in the presence of chloride ion. The loss of SMX increased monotonically upon addition of chloride ion. Mineralization was not inhibited in the early stages of oxidation, but the formation of chlorinated intermediates greatly increased the charge needed for complete mineralization. The oxidation of SMX (with or without chloride) could not be studied at Ti/IrO_2–Ta_2O_5 anodes, which were rapidly inactivated due to electropolymerization through the aniline functional group. The present study was therefore initiated to remedy this limitation; the substrate selected was acetaminophen (AP), which has previously been shown to undergo oxidation in the absence of chloride at both active (Ti/IrO_2–Ta_2O_5) and inactive (BDD) anodes using a plug-flow divided reactor.[23] AP offers a useful mechanistic distinction: whereas mineralization occurs smoothly at the inactive anode BDD, the chief product at the active anode Ti/IrO_2–Ta_2O_5 is benzoquinone (BQ).[23,24] Brillas et al.[25] studied the mineralization of AP in the pH range of 1–12 with Na_2SO_4 as supporting electrolyte using an undivided cell. Complete mineralization with release of NH_4^+ and NO_3^- ions was achieved at a BDD anode, but mineralization was inefficient at Pt.

Materials and methods

Materials

Acetaminophen, *N*-(4-hydroxyphenyl)ethanamide (AP), 1,4-benzoquinone (BQ) 98%, potassium iodide 99%+, and sodium perchlorate 99%+ were supplied by Sigma-Aldrich (Oakville, ON). HPLC grade acetonitrile was obtained from Caledon Laboratories (Georgetown, ON); sodium chloride, sodium phosphate monobasic monohydrate, and sodium hydroxide were supplied by Fisher Scientific Company (Toronto, ON). "Ultra" bleach (6%) was purchased from No-Frills, Guelph ON, subsidiary of Loblaws Inc, Toronto, ON. Solutions were prepared using a Millipore Milli-Q Reagent Water System with water having resistivity of about 18.2 MΩ cm. The Si/BDD anodes were obtained from the Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel; titanium served as the cathode (Chemistry machine shop, University of Guelph).

Apparatus and experimental procedures

Batch electrolyses were performed in a 150 mL beaker (Pyrex, USA) with a solution volume of 100 mL of 1 mmol/L AP or BQ; ionic strength was maintained at 0.1 mol/L with $NaClO_4$. The immersed areas of both the titanium cathode and the Si/BDD anode were 3.75 cm^2. Solutions were stirred during electrolysis using a Thermix stirrer (Fisher Scientific Model 120 MR). Voltage, electrode potential, and current were monitored using a Wavetek DM5XL Voltmeter and Mastercraft 052–0060–2 multimeter. Power to the electrochemical reactor was supplied by an EG&G Model 363 potentiostat/galvanostat. Cyclic voltammetry measurements were carried out at room temperature in a 50 mL beaker (solution volume 40 mL) using a BDD MDA 5–150/106 microelectrode array (Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel) as the working electrode, platinum plate as the counter electrode, and saturated calomel reference electrode (Fisher Scientific, Toronto. ON). Data were obtained using an EG&G Model 273 Potentiostat/Galvanostat at a fixed sweep rate of 50 mV s^{-1}, controlled using Power Suite version 2.12.1 software. Chemical hypochlorination was performed in a 150 mL beaker with a solution volume of 100 mL and a concentration of 1 mmol/L AP or BQ; injections of 40 μL bleach were added every 10 min. The bleach was standardized by iodometry: nominal concentration 6% *w/v*; actual 6.4%, 0.86 mol/L.

Analytical measurements

The reactions were followed by HPLC, using a Waters 600E system equipped with a Waters 2487 dual λ absorbance detector set at 254 nm and a Supelco Discovery C18 column 150 × 4.6 mm (5 μm) equipped with a silica pre-column guard. An HPLC method was developed by using a mobile solvent of acetonitrile–water (30:70) (filtered through a 0.2 μm filter) at a flow rate of 1.0 mL min^{-1} (retention times

of AP and BQ were ~2.5 min and ~4.0 min, respectively). Samples were manually injected into the 20 μL sample loop of a Rheodyne injector. Total Organic Carbon (TOC) was analyzed as non-purgeable organic carbon (NPOC) with a Shimadzu TOC analyzer, model TOC-VCPN. Absorbable organic halide (AOX) analysis was provided by ALS Laboratory Services of Thunder Bay, ON, Canada.

Results and discussion

Voltammetry

Cyclic voltammetry of AP at a 5–150/106 BDD microelectrode array (Fig. 1) showed an irreversible voltammetric peak at +0.94 V vs. SCE with I_p α [AP], in both the absence and presence of 100 mmol/L NaCl. Although E° for oxidation of chloride ion to HOCl is +1.49 V and for ClO^- is 0.90 V,[26,27] there was no oxidation current for solutions of chloride alone, because of the large overpotential for this oxidation.[28,29] There was no oxidation current for *p*-benzoquinone (an oxidation product of AP) in the region of water stability nor did we observe the reduction peak for the immediate oxidation product of AP (*N*-acetylbenzoquinonimine) that had been observed by Nematollahi et al.[30] on a glassy carbon working electrode, Madsen et al[31] on porous graphite, or Van Benschoten et al.[32] on carbon paste. At Ti/RuO_2, the current at ~ +1.2 V vs. SCE due to solvent oxidation obscured the oxidation of AP itself (see Fig. 1 in the Supplementary data).

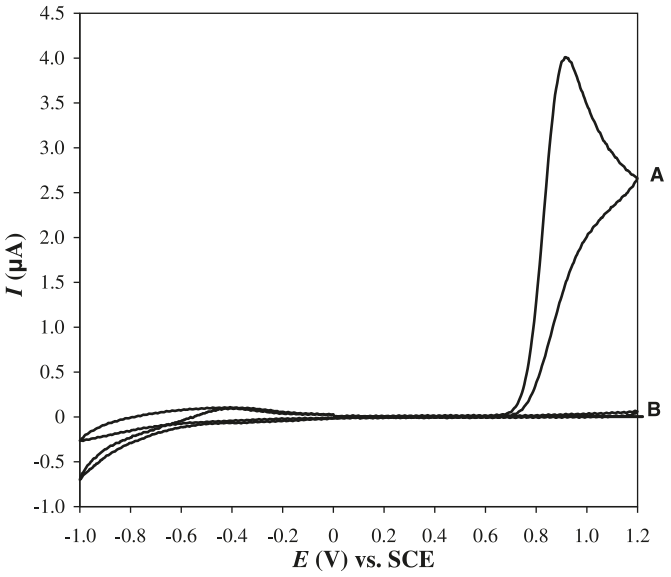
Potentiostatic oxidation of AP in the presence of chloride ion

The oxidation of 1 mmol/L AP at Si/BDD was followed by HPLC within the range of water stability at +1.4 V vs. SCE, using 100 mmol/L $NaClO_4$ or NaCl as the supporting electrolyte in a divided cell. The loss of AP was very slow, whether or not chloride was present (Fig. 2A). Initial rates were 0.13 μmol min^{-1} ($NaClO_4$) and 0.10 μmol min^{-1} (NaCl). The current was too low to be recorded accurately. No anode gas was observed, showing that there was no discharge of water at this potential and hence no production of hydroxyl radicals. The reaction was therefore attributed to direct oxidation of AP (pathway (*i*)). This conclusion was supported by the formation of a significant yield of benzoquinone, which is rapidly destroyed by hydroxyl radicals (1.2×10^9 L mol^{-1} s^{-1} at pH 7).[33] At Ti/RuO_2, the reaction was much faster because water is oxidized at this active anode, giving the surface oxide RuO_3, which can oxidize either AP directly or Cl^- to hypochlorite; as a result, the loss of AP was faster in the presence of chloride (Fig. 2B). No mineralization occurred in any of these reactions.

Amperostatic oxidation of AP

The electrochemical oxidation at 80 mA of AP at Si/BDD and at Ti/RuO_2 in the absence of chloride ($NaClO_4$ supporting electrolyte) is presented in Fig. 3, in which all data are shown in parts per million (mg L^{-1}) of carbon. The loss of AP was slightly slower at Ti/RuO_2 and in both cases followed kinetics intermediate between pure current control (linear relationship between the concentration of AP remaining and time), and mass transport control (exponential loss of AP with time), tending to the latter towards the end of the reaction. Figure 2 in the Supplementary data shows the progress of the reaction according to the half-order kinetic model (between current control and mass transport control) developed in our previous work on the oxidation of sulfamethoxazole.[34]

Fig. 1. Cyclic voltammogram (0 V to +1.2 V to –1.0 V to 0 V) for 1 mmol/L AP at Si/BDD microelectrode array; sweep rate 50 mV s^{-1}; supporting electrolyte 100 mmol/L $NaClO_4$. (A) AP; (B) solvent.



Kapalka et al.[8] propose that for mass-transport limited reactions at inactive anodes such as BDD, the substrate undergoes multiple acts of $HO^•$-induced oxidation without migrating from the anode into the bulk solution. At its extreme, this kinetic behaviour implies loss of substrate in parallel with loss of TOC. This was broadly true for the oxidation at BDD, where Fig. 3 shows that the course of mineralization, monitored as NPOC, only slightly lagged behind the loss of AP. (The deviation between the rates should be greater under pure current control, when the concentration of $HO^•$ radicals at the anode is insufficient to prevent migration of intermediates into the bulk solution.) The loss of AP was somewhat slower at Ti/RuO_2 but mineralization did not occur, consistent with oxidation at this active anode being a two-electron process; the observed formation of BQ supports this conclusion.

The presence of 100 mmol/L chloride ion greatly accelerated the loss of AP at both BDD and Ti/RuO_2 (Fig. 4), consistent with the involvement of EH. These reactions were first order in concentration of AP indicating that the principal electrochemical reaction is formation of FAC, followed by reaction between FAC and AP in the bulk solution. Mineralization occurred more slowly at the BDD anode when chloride was present (compare Figs. 3 and 4). AOX analysis showed the formation of chlorinated byproducts (Fig. 5), which were also detectable (though not specifically identified) by HPLC (see Fig. 3 in the Supplementary data, Panels A–C). Figure 5 shows the losses of AP and NPOC in mmol/L of carbon, and progression of AOX in mmol/L of chlorine. Under these conditions, mineralization could be initiated by hydroxyl radical attack on AP, with subsequent chlorination,

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Fig. 2. Potentiostatic electrolysis of 1 mmol/L AP at +1.4 V (vs. SCE). Panel A: Si/BDD anode; panel B: Ti/RuO_2 anode. Symbols: ◇, AP; ○, BQ in 100 mmol/L $NaClO_4$; ◆, AP; ●, BQ in 100 mmol/L NaCl.

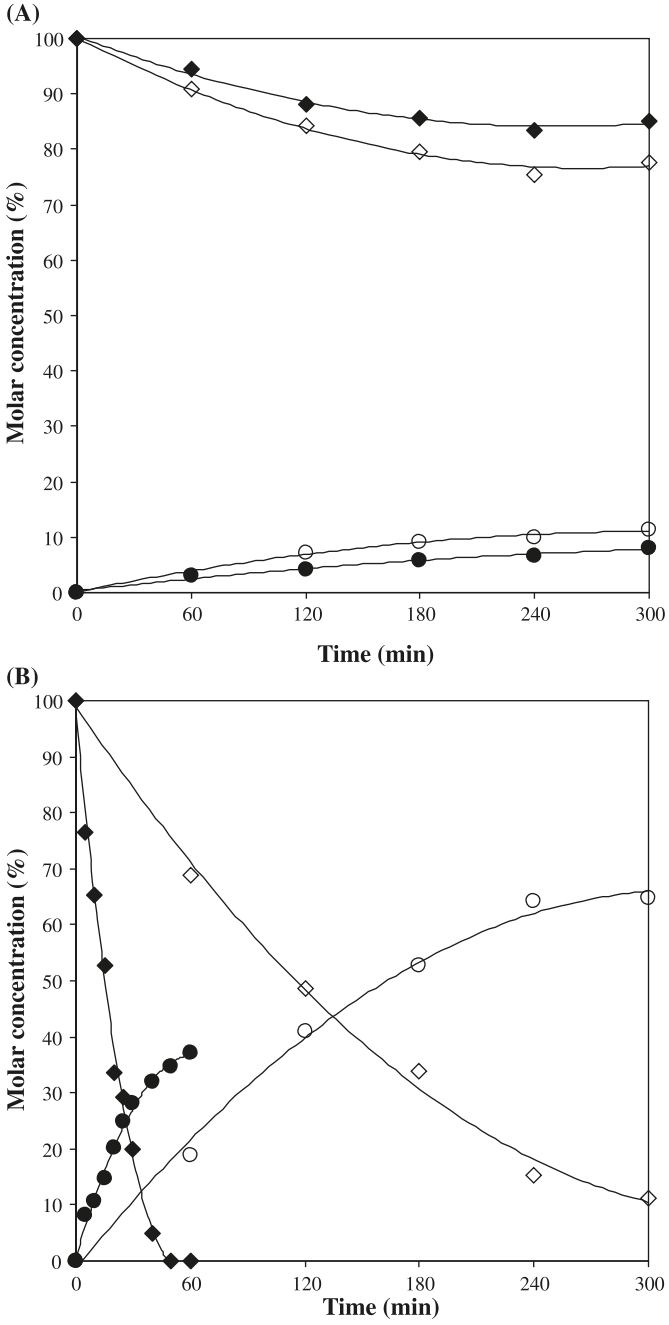
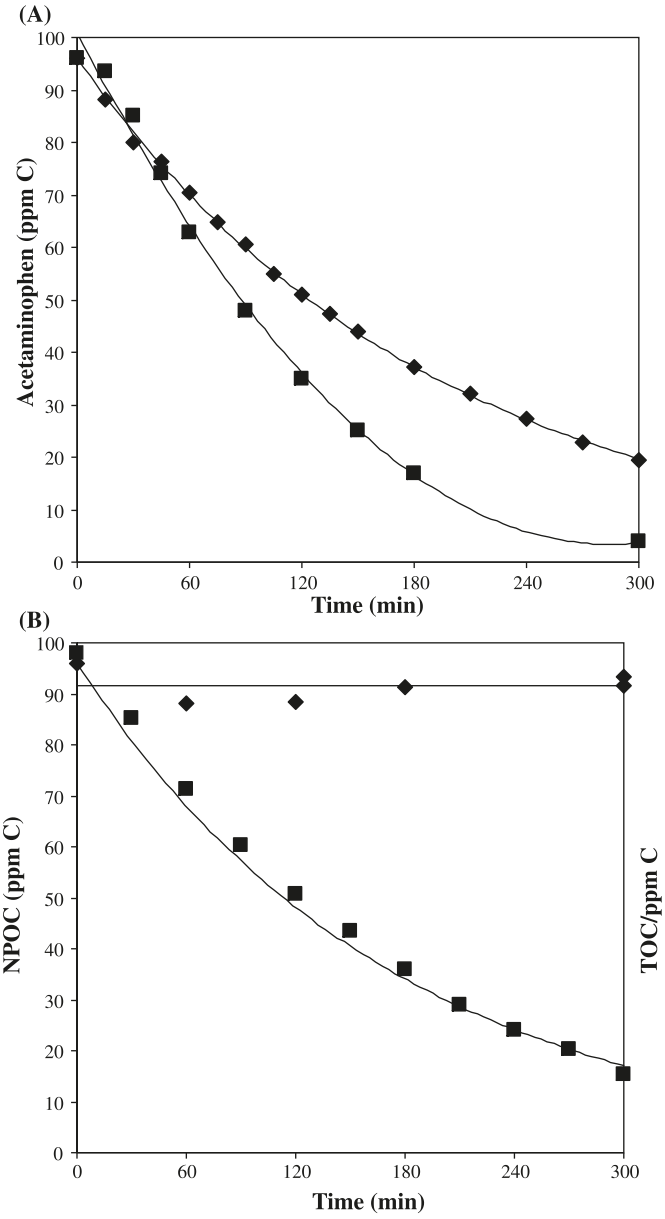


Fig. 3. AP and NPOC loss during electrolysis at Si/BDD and Ti/RuO_2 anodes in the absence of chloride. Panel A: AP; panel B: NPOC. Symbols: ■, Si/BDD anode; ◆, Ti/RuO_2 anode. Supporting electrolyte: 100 mmol/L $NaClO_4$; initial AP concentration: 1 mmol/L; current: 80 mA.



and (or) by an initial hypochlorination and subsequent reaction with hydroxyl radicals. The mechanistic picture is further complicated by suggestions that adsorbed chloro and oxychloro radicals could participate in the oxidation process, though there appears to be no direct evidence for the intermediacy of these species.[35–39]

The chlorinated products were highly persistent; Fig. 5 shows that by the end of the electrolysis, the remaining organic material contained an average of one chlorine atom for every three carbon atoms. Complete mineralization of AP in the presence of chloride is thus much more energy-demanding than the corresponding chloride-free reaction (see Fig. 4 in the Supplementary data), as found previously for SMX.[22] The apparent partial mineralization of AP in the chloride-assisted oxidation at Ti/RuO_2, shown in Fig. 4, Panel B, is an experimental artefact, caused by the fact that our TOC analyzer actually measures non-purgeable organic carbon (NPOC) rather than TOC. When correction was made for the purgeable organic carbon, it was found that no mineralization had occurred (see later for discussion of this point). These results support the hypothesis that at Ti/RuO_2 the principal reaction pathway is hypochlorination, whereas at BDD there is competition between EH and EAOP, with the initial products of EH being susceptible to EAOP and

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Fig. 4. AP and NPOC loss during electrolysis at Si/BDD and Ti/RuO_2 anodes in the presence of 100 mmol/L NaCl. Panel A: AP; panel B: NPOC and TOC. Symbols: ■, Si/BDD anode; ◆, Ti/RuO_2 anode; TOC: ◇, Ti/RuO_2 anode; supporting electrolyte. Initial AP concentration: 1 mmol/L; current: 80 mA.

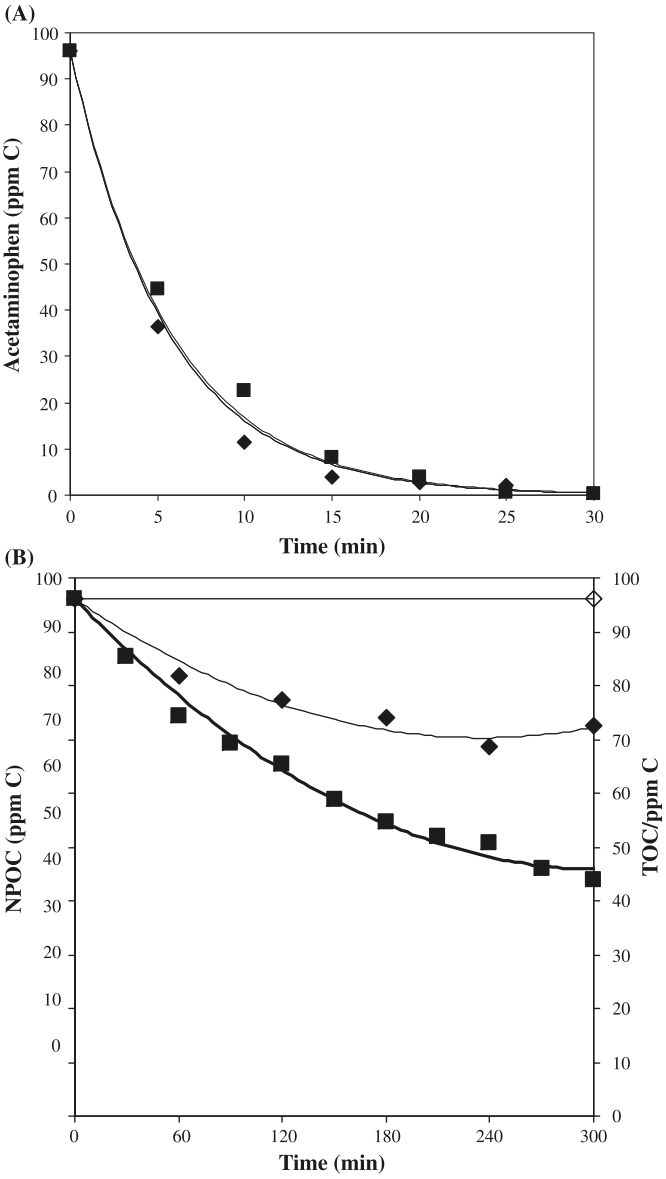
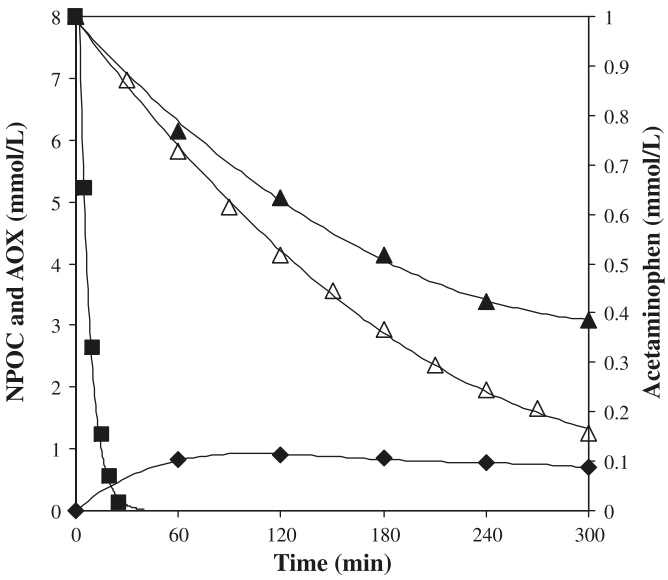


Fig. 5. Electrolysis of 1 mmol/L AP with a Si/BDD anode at 80 mA in the absence and presence of chloride. Δ, NPOC in the absence of chloride (100 mmol/L $NaClO_4$); ■, AP; ▲, NPOC; ◆, AOX, all in the presence of 100 mmol/L NaCl.



vice versa. The latter hypothesis is supported by the observation that at BDD the loss of AP accelerated with increasing Cl^- concentration, whereas the initial rate of mineralization was almost unaffected (see Fig. 5 in the Supplementary data; current 20 mA). At higher current, the initial loss of AP was faster (see Fig. 6 in the Supplementary data; current 80 mA), although the efficiency of mineralization per unit charge was lower, owing to more parasitic oxidation of water to O_2 (see Fig. 7 in the Supplementary data).

Electrooxidation of AP in the presence of chloride ion was compared with conventional chemical hypochlorination via FAC. Previously, Pinkston and Sedlak[40] showed that the pseudo first-order rate constant for reaction of AP with FAC changed by less than one log unit over the range pH 5–10. Bedner and MacCrehan[41] identified two initial reaction pathways: ring chlorination and oxidation to *N*-acetylbenzoquinonimine (and hence benzoquinone). We found that chemical hypochlorination was efficient on the basis of mol AP lost per mol FAC added (see Fig. 8 in the Supplementary data). No mineralization was observed, similar to the electrolysis at Ti/RuO_2 although the pattern of byproducts observed (see Fig. 3F in the Supplementary data) differed from those produced electrochemically at either Si/BDD or Ti/RuO_2 (see Fig. 3C and 3E in the Supplementary data). As in the electrochemical experiments, NPOC suggested that mineralization had occurred, but the missing material was again traceable to purgeable organic carbon (POC). The level of POC increased if NaOCl was added portion-wise (to mimic its electrochemical formation) rather than in a single aliquot, or if the solution pH was lowered from 6 to 5 (see Fig. 9 in the Supplementary data). We considered whether the purgeable material might be due to hydrolysis of the acetyl side chain of AP to acetate, but concluded that this was not the explanation because acetic acid was not purgeable under our analytical conditions.

Because chemical hypochlorination is a common strategy for waste treatment,[42–49] we carried out a series of experiments to explore whether electrochemical oxidation could be useful for remediation after hypochlorination with FAC. The efficiency of mineralization was greater when $NaClO_4$ was used as the supporting electrolyte in the post-treatment rather than NaCl. However, mineralization remained most effective in the absence of chlorination (Fig. 6).

Amperostatic oxidation of BQ

Previous work has shown that *p*-benzoquinone (BQ) is an intermediate in the oxidation of AP. Parallel to the metabolic chemistry of AP, the formation of BQ is believed to involve a two-electron oxidation of AP to a quinonimine followed by hydrolysis (Scheme 1).[30,32]

Yields of BQ are high when AP is oxidized at active electro-

Scheme 1.

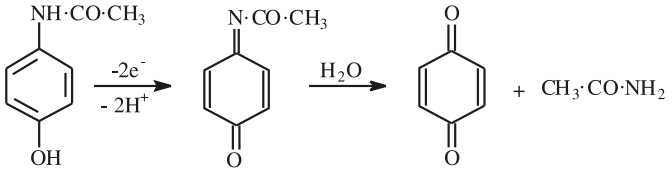
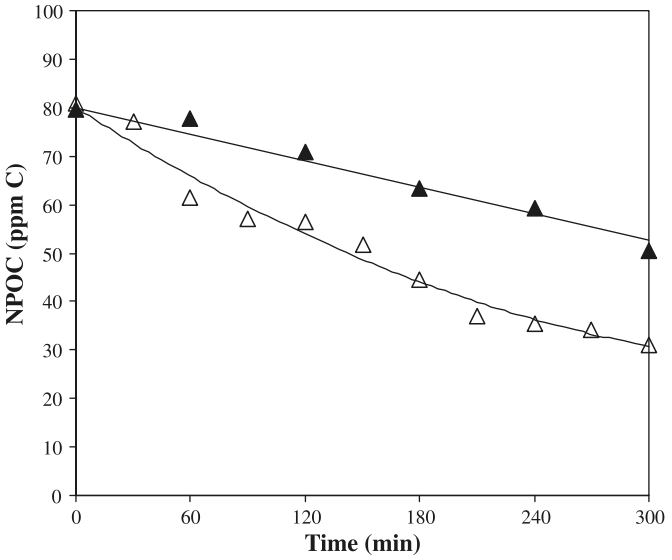


Fig. 6. Comparison of chemically hypochlorinated AP and subsequent electrolysis with Si/BDD at 80 mA. Electrolysis of pre-hypochlorinated AP: Δ, AP with 100 mmol/L $NaClO_4$; ▲, AP with 100 mmol/L NaCl; initial AP concentration: 1 mmol/L.



des, but low to negligible at inactive electrodes such as Si/BDD.[23–25] However, the formation of even low yields of BQ is less easily explained at an inactive anode such as Si/BDD, because Yang et al.[50] have indicated that addition to the phenolic ring is the primary reaction between AP and HO•. The voltammetric data reported above suggest that the low yield of BQ may arise by competing direct oxidation of AP. However, BQ is very susceptible to radical addition reactions and cannot build up to high concentrations when inactive anodes are used.

The voltammetric data also indicate that BQ should be stable to further oxidation at active electrodes, and this was essentially the case in earlier work carried out in a flow cell.[23,24] However, in the present work, which employed undivided batch reactors, BQ was at least as susceptible to reaction as AP at both Si/BDD and Ti/RuO_2 (see Fig. 10 in the Supplementary data). This phenomenon was traced to two factors: reduction of BQ at the cathode of the undivided cell and greater chemical stability at lower pH. Figure 7 demonstrates increased persistence of BQ upon electrolysis at Ti/RuO_2 in the order: undivided cell using $NaClO_4$ supporting electrolyte < undivided cell using H_2SO_4 supporting electrolyte(pH 2) < divided cell using H_2SO_4 supporting electrolyte (pH 2) .

In many respects, the mineralization of BQ in the undivided batch reactor paralleled that of AP (compare Fig. 8 with Figs. 3 and 4). The rate of disappearance of BQ was comparable at Ti/RuO_2 and Si/BDD in the absence of chloride. Mineralization closely followed BQ loss at Si/BDD, but

Fig. 7. Electrolysis of 1 mmol/L *p*-benzoquinone with a Ti/RuO_2 anode at 80 mA. Symbols: ■, undivided cell (100 mmol/L $NaClO_4$); ◆, undivided cell (H_2SO_4, pH 2); ▲, divided cell (conc. H_2SO_4, pH 2).

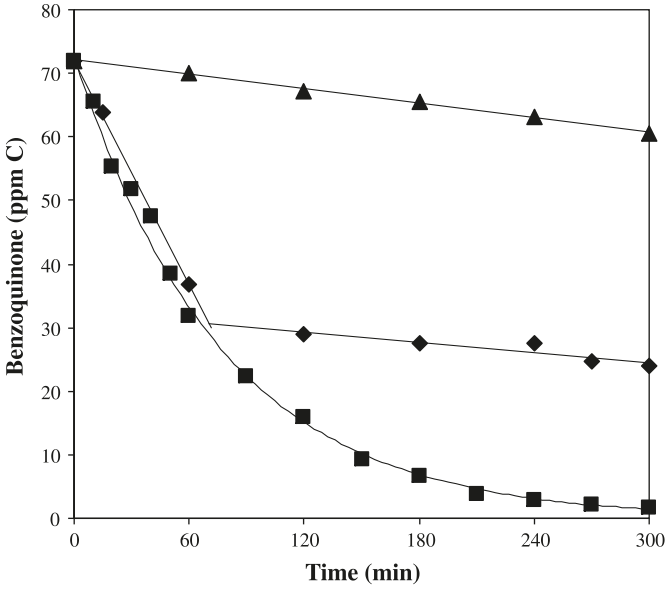
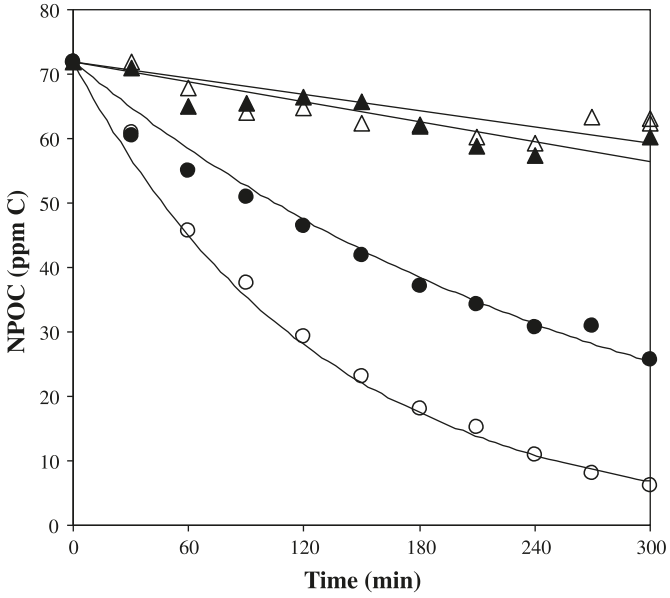


Fig. 8. NPOC loss during electrolysis of BQ with Si/BDD and Ti/RuO_2 at 80 mA in the absence and presence of chloride in an undivided cell. Si/BDD: ○, 100 mmol/L $NaClO_4$; ●, 100 mmol/L NaCl; Ti/RuO_2: Δ, 100 mmol/L $NaClO_4$; ▲, 100 mmol/L NaCl; initial BQ concentration: 1 mmol/L.



there was almost no mineralization (based on NPOC) at Ti/RuO_2. BQ is highly susceptible to hypochlorination, and in the presence of chloride, the rate of reaction at Ti/RuO_2 was greatly increased but again there was no mineralization. At Si/BDD, the presence of chloride increased the reactivity of BQ but substantially decreased the rate of mineralization; analysis by HPLC showed the presence of chlorinated byproducts.

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Conclusions

We introduced this work by identifying four distinct pathways for the electrochemical oxidation of an organic substrate, namely, (*i*) direct electron transfer from the substrate to the anode, (*ii*) EAOP by reaction of substrate with $HO^{\bullet}$ at inactive anodes, (*iii*) non-radical (two electron) oxidation of substrate by MO_{n+1} at active anodes, and (*iv*) EH if Cl^- is present.

Acetaminophen is a valuable substrate for distinguishing these mechanisms. Its distinct voltammetric oxidation peak allowed the study of its direct electron transfer in the region of water stability. This reaction does not lead to mineralization in the absence or presence of chloride, even at the inactive anode Si/BDD, because hydroxyl radicals are not formed. It is inconveniently slow as a prospective remediation technology and rather inefficient; this mechanism probably contributes little to the overall chemistry except in the range of water stability.

Amperostatic oxidation in the region of water decomposition (O_2 evolution at the anode) showed an efficient mineralization reaction by the EAOP mechanism at Si/BDD in the absence of chloride; low yields of BQ at intermediate stages of the reaction were ascribed to the competing direct electron-transfer reaction. Comparison between chemical hypochlorination (FAC) and electrochemical oxidation at Ti/RuO_2 indicated that the latter process, which does not lead to mineralization, principally involves mediated hypochlorination. Oxidation at Si/BDD in the presence of chloride is the most complex mechanistically, with competition between EAOP and EH. Kinetic analysis suggested that chloride ion diverts the main pathway for initial destruction of AP to hypochlorination in the bulk even at BDD; this was confirmed by rather similar patterns of chlorinated byproducts at both electrodes. In contrast, different patterns of chlorinated byproducts were seen at Si/BDD and Ti/IrO_2–Ta_2O_5 in the degradation of SMX.[22] Even though EH appears to be the initial reaction for loss of AP, crossover between the EH and EAOP reaction sequences is evident by the occurrence of mineralization, albeit more slowly than in the absence of chloride.

Critically for the use of electrochemical oxidation in waste management, the presence of chloride ion as a constituent of the waste leads to the formation of persistent byproducts, whose removal significantly increases the energy requirement for complete mineralization at the inactive anode BDD (although the initial rate of mineralization is not retarded by chloride ion at low current). Although electrolysis can be considered as a post-treatment to the common industrial practice of chemical hypochlorination, mineralization under those circumstances is more energy-demanding.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5367. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml.

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